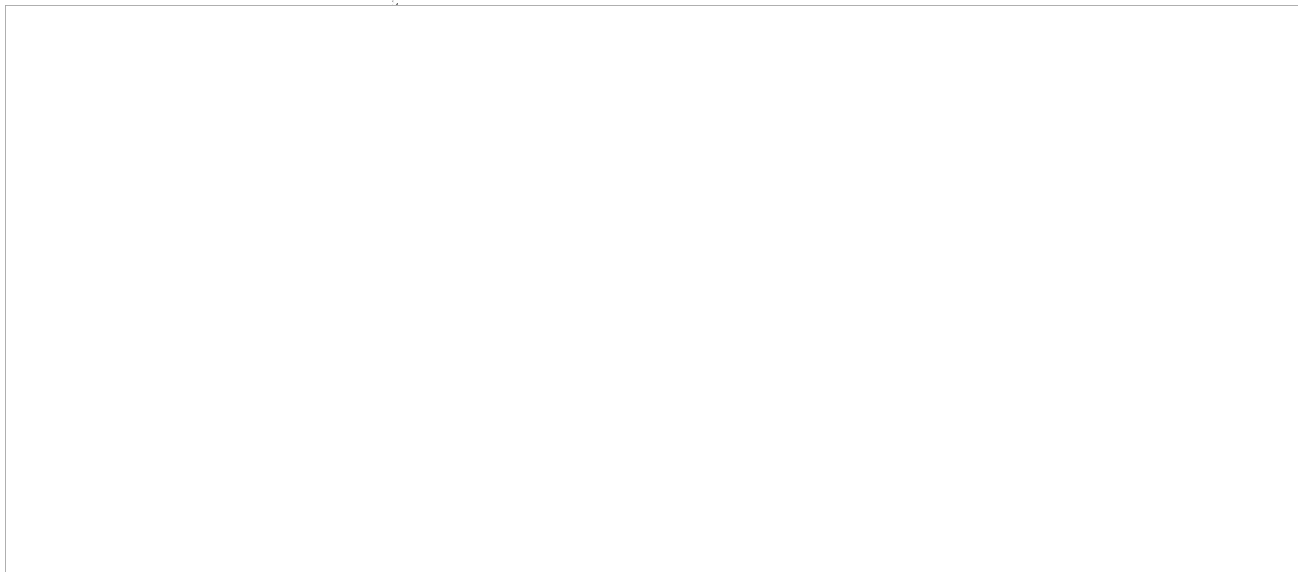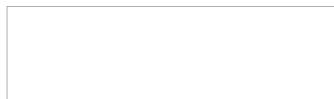50X1-HUM

THE EFFECTIVE MASS OF THE POLARON

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THE EFFECTIVE MASS OF THE POLARON

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Summary

It is proposed that the current-carrier in crystals with ionic lattice is not the zonal conductance electron, but the polaron. The conservative motion of the polaron is considered as a whole. The energy of the system is given as a function of the polaron's forward motion; the polaron's equation of motion in an external field is also found.

Introduction

The present theory of electron conduction in dielectrics and semi-conductors assumes that the conductance electron moves in one of the "permissible" energy zones of the crystal, but the electron's wave-function (psi-function) represents a wave whose amplitude is constant in the whole volume of the crystal. The presence in the crystal of for-bidden zones is experimentally verified: this is borne out by the very fact of the existence of dielectrics, by studies on the temperature de-pendence of electrical conductivity, by the internal photoeffect, by photoeffect of metals in dielectrics, etc. Other characteristic features of this theory have not found direct experimental confirmation, but sometimes even contradict known experimental facts.

But first of all (at least for ionic crystals) it is necessary to indicate the internal contradictions of the present theory; namely, usually in a discussion of the quantum states of a conductance electron it is assumed that the ions are held fast at the nodes of the lattice; in this situation the electron is in a periodic field. Actually, however,

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the ions move and the electron's state follows adiabatically the motion
of the ions. S.I. Pekar considered such a motion [1] and showed
that a conductance electron by its own electrical field will dielectrically
polarize an ionic crystal. It turns out that even in the very beginning
of the polarization process a polarized crystal presents for an electron
a potential hole with discrete spectrum; but the electron, having spent
part of its energy in polarization of the crystal, passes to a discrete
level in a local state; thereupon polarisation of the crystal is inten-
sified, but the electron's level and the energy of the entire system
are lowered. Equilibrium sets in when the energy of the entire system
reaches a minimum; in this situation is formed the polaron, which was
considered in detail by one of the authors in previous works [2, 3].
Thus the zonal state of a conductance electron does not correspond to
an extremum of the system's energy; that is, the state is unstable.
Slow conductance electrons must continuously pass to the polaron state.
The time of collapse for the zonal state of a slow electron must be of
the order of 10^{-13} second; consequently it is necessary to reconsider
the fundamentals of the existing theory of conductance.

S.I. Pekar [1, 4] expressed a new point of view on the electron
conductivity of ionic crystals, according to which (point of view) the
current-carrier is the polaron and not the free electron in a zone of
conductivity. A polaron in an external electrical field must move like
a negative charge; in this situation the entire local state as a whole
must be displaced or shifted along the field (the inertial polarization
of a crystal must follow the polaron's movement). The calculated mobility
of a polaron [4], in respect to its order of magnitude, exactly agrees
with the mobility of a current-carrier as determined experimentally and
equals the product of electrical conductivity times the Hall constant.

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The Effective Mass of the Polaron

o In the dielectrical polarization of an ionic crystal one can dis-
tinguish an inertial and a non-inertial part [2]. The non-inertial
part of polarization is characterized by the square of the index of re-
fraction of light (in the region where the dispersion curve has a plat-
eau); it is assumed that this part follows completely the motion of the
conductance electron. As a result of the non-inertial polarization of
the crystal's nodes by an electron's field this electron is acted upon
by an additional force which (force) possesses the periods of the lattice;
this force we shall include in the total periodic potential of the electron
in the crystal. In order to solve future problems one can utilize the
well known method of the effective mass of an electron [5]; that is,
one can ignore periodic potential by replacing at once the electron's
mass by the equivalent mass m: μ .

The assumptions that the electron's state $\psi(\vec{r}, t)$ follows
adiabatically the motion of the ions and also that the radius of the psi-
state (Schroedinger or wave state) exceeds the lattice constant lead
to the following expression for the energy H of the system:

$$H = (\hbar^2/2\mu)\int |\nabla \psi|^2 d\tau - \int \vec{p}\,\vec{D}[\psi]\,d\tau + U_p \tag{1}$$

Here $\vec{p}(\vec{r}, t)$ is the inertial part of the specific polarization of a
dielectric [2]; and

$$\vec{D}[\psi] = e\int |\psi(\vec{r}_1)|^2 \{(\vec{r} - \vec{r}_1)/|\vec{r} - \vec{r}_1|^3\}\, d\tau_1 \tag{2}$$

is the quantum-mechanical mean-value of the electrostatic induction
of the electron. In Formula (1) the first term represents the kinetic
energy of the electron, and the second form represents the energy of
interaction between electron and polarized crystal; but Up is the total
energy of the crystal under the assumption that the electron is
suddenly expelled (remote)-namely, Up is the potential and kinetic energy
of the ions.

*Note: Letters with arrows, $\vec{r}$, $\vec{v}$, $\vec{D}$ etc, are vectors.

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In accordance with the variational principle of quantum mechanics (which principle replaces the Schroedinger equation), the expressions $\vec{P}(\vec{r},t)$ and $\psi(\vec{r},t)$ are determined, for each assigned polarization, as the minimum of the functional (1), with the additional condition:

$$\int |\psi|^2 d\tau = 1 \tag{3}$$

consequently

$$(\hbar^2/2\mu)\, \delta \int |\nabla\psi|^2 d\tau - \int \vec{P}\, \delta \vec{D}[\psi] d\tau = 0 . \tag{4}$$

Furthermore let us assume that psi is already determined in this manner; then H is the Hamiltonian function, which describes the motion of ions in a crystal.

Let us assume that the crystal is a system of ions executing small harmonic oscillations and let us express H by suitable normal coordinates and velocities of the ions. The motion of the ions is determined by the ordinary canonical Hamiltonian equations. (Equation (4) must be taken into account in the differentiation of H.) These latter equations are equations of the forced oscillations of ions under the action of the force $\vec{D}(\vec{r},t)$.

Let us consider the partial case of a motion where the polaron moves forward as a whole with the vector-velocity $\vec{v}$; that is, where:

$$\psi = \psi(\vec{r}-\vec{v}t), \quad \vec{D} = \vec{D}(\vec{r}-\vec{v}t), \quad \vec{P} = \vec{P}(\vec{r}-\vec{v}t). \tag{5}$$

Expanding $\vec{D}$ and $\vec{P}$ into Fourier series

$$\vec{D} = \sum_k \vec{D}_k\, e^{i\vec{k}(\vec{r}-\vec{v}t)} = \sum_k \vec{D}_k\, e^{i(\vec{k}\vec{r}-\omega_k t)} \tag{6}$$

$$\vec{P} = \sum_k \vec{P}_k \cdot e^{i(\vec{k}\vec{r}-\omega_k t)} \quad (\text{where } \omega_k = \vec{k}\vec{v}), \tag{7}$$

we note that the forced oscillations of ions that are due to the force $\vec{D}$ can be obtained as a simple superposition of oscillations which are caused by definite harmonics of the form:

$$\vec{D}_k \cdot e^{i(\vec{k}\vec{r}-\omega_k t)} \tag{8}$$

These harmonics, of course, are not ordinary electro-magnetic waves

(the velocity is $v \neq c$; they have another law of dispersion; and they are not transverse). Since, however, the polaron's dimensions exceed the lattice constant there will predominate in Fourier Expansion (6) harmonics whose wavelength also exceed the lattice constant. In this case the problem reduces to the well known definite case of long waves and one can, in a discussion of the forced oscillations of ions, replace the harmonics (8) by electromagnetic waves whose induction vector has the same amplitude and frequency. This substitution permits one to express the polarization of a dielectric by a dielectric constant $\varepsilon(\omega)$ that determines the dispersion of electromagnetic waves in a crystal:

$$\vec{P_k} = \frac{1}{4\pi} C(\omega_k) \vec{D_k} \quad \text{and} \quad C(\omega) = \frac{1}{n^2} - \frac{1}{\varepsilon(\omega)} . \tag{9}$$

It is necessary to keep in mind, in drawing conclusions from the expression for $C(\omega)$, that $\vec{P}$ is merely the inertial part of specific polarization [2]. It is assumed that the crystal is polarized isotropically.

The relations (9) are the solution for the equations of forced oscillations. Equations (2), (4), (9) determine the functions $\vec{D}$, $\vec{p}$, and psi (wave-function). Obviously all three equations can satisfy simultaneously functions of the form (5).

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$$C(\omega_k) = c_0 + c_2 \omega_k^2 + \cdots \tag{10}$$

where $c_0 = \frac{1}{n^2} - \frac{1}{\varepsilon(0)}$ and $c_2 = \frac{c_0}{\omega_l^2}$; (11)

here ω_l is the limiting frequency of the optical oscillations of the ions (which must not be confounded with "frequency of dispersion").

Since we have:

$$\omega_k^2 \vec{D_k} e^{i(\vec{k}\vec{r} - \omega_k t)} = -\frac{\partial^2}{\partial t^2} \vec{D_k} e^{i(\vec{k}\vec{r} - \omega_k t)} \tag{11'}$$

it is convenient to write the equations of forced oscillations (9) in a 'summed' form:

$$\vec{p}(\vec{r}, t) = \frac{1}{4\pi} \left[c_0 \vec{D}(\vec{r}, t) - c_2 \frac{\partial^2 \vec{D}}{\partial t^2} \right]. \tag{12}$$

In order to determine the effective mass of a polaron it is necessary to calculate the energy (1) with an accuracy up to terms of the order v^2. Keeping this in mind and the oddness of $\varepsilon(\omega)$ (we disregard absorption; ie the imaginary part of $\varepsilon(\omega)$, $\Im \varepsilon(\omega)$), we set up $C(\omega)$ in the form of a series:

- 5 -

Now it is easy to obtain the expression for the energy Up of a crystal. Keeping in mind that the work performed per unit time on unit volume of a crystal is:

$$\vec{D} \cdot \vec{p} = \frac{\vec{D}}{4\pi} \cdot [c_0 \vec{D} - c_2 \ddot{\vec{D}}]$$
(13)

and setting the energy of a unit volume equal to zero when there is no field (that is when the polaron is far away), we obtain:

$$U_p = \frac{c_0}{8\pi} \int \vec{D}^2 d\tau + \frac{3c_2}{8\pi} \int \dot{\vec{D}}^2 d\tau .$$
(14)

Substituting (12) and (14) into the expression for the energy of the system (1), we obtain:

$$H = \frac{\hbar^2}{2\mu} \int |\nabla \psi|^2 d\tau - \frac{c_0}{8\pi} \int \vec{D}^2 [\psi] d\tau + \frac{c_2}{8\pi} \int \dot{\vec{D}}^2 [\psi] d\tau .$$
(15)

The case for an immobile polaron (namely, $v=0, \vec{D}=0$) was discussed in detail by one of the authors in previous works [2, 3]. There was obtained the ground state of the polaron: $\psi = \psi_0 (\vec{r})$ and the corresponding energy:

$$H_0 = -0.0547 (\mu e^4/\hbar^2) c_0^2$$
(16)

Taking this solution as the zero approximation and passing to the case of a uniformly moving polaron, one can show that the wave-function and the energy receive small corrections if the velocity satisfies:

$$v \ll r_m \omega_1$$
(17)

where r_m is the radius of the polaron [2].

The energy is written, with an accuracy up to terms of the order v^2, in the form:

$$H = H_0 + \frac{1}{2} M v^2 , \qquad M = \frac{c_2}{3}\left[\int_0^\infty \left(\frac{\partial}{\partial r}\vec{D}[\psi_0]\right)^2 r^2 dr + Q^*\right]$$
(18)

If we insert D $[\psi_0]$ from [3], the effective mass of the polaron turns out to equal:

$$M = 5.8 \cdot 10^{-3} \left(\frac{\mu e^2}{\hbar^2}\right)^3 e^2 c_0^2 c_2^3 = 9.08 \cdot 10^3 \frac{\mu^3}{m^3} c_0^3 c_2 \; grams$$
(19)

where m is the mass of a free electron and μ is the effective mass of an electron in an old conductivity zone. Ordinarily M is

$$* NOTE: \quad Q \equiv 2 \int_0^\infty D^2[\psi_0] dr$$

- 6 -

considerably greater than the mass of an electron (for NaCl crystal it is 432 times greater).

Taking into consideration the motion of a polaron in an external electrical field $\vec{E}$ and comparing the power generated by this field with the increment in energy (18) per second, we obtain for a polaron the ordinary equation of motion

$$M\vec{v} = e\vec{E}. \tag{20}$$

It is assumed above that the uniform motion of a polaron is conservative; that is, that the harmonics (8) sustain the stationary forced oscillations of the ions, but do not generate natural oscillations (heat is released). In this situation occurs a certain damping of the polaron. The energy released by a polaron to the lattice can be formally calculated as the adsorption in the crystal of the above-mentioned electromagnetic waves equivalent to the harmonics (8). Such a calculation showed that the damping force is proportional to the velocity, but the mobility of the polaron in an external field equals:

$$\text{(mobility)} \quad u = 0.262 \cdot 10^{-13} \frac{E(o)^{3/2}}{b\mu^3 m^{-3} c_0^3} \quad \text{absolute units.} \tag{21}$$

The coefficient k is determined experimentally by measuring the adsorption of electromagnetic waves in a crystal: namely, $-b\omega$ is the imaginary part of the index of refraction of a crystal for waves with a frequency $\omega \ll \omega_1$. The damping force $\vec{R}$ is expressed in terms of mobility and speed of a polaron by the following formula:

$$\vec{R} = -\frac{e\vec{v}}{u}. \tag{22}$$

Disregarding weak damping and quantizing the polaron's motion as a whole (without a field), one can be convinced that the motion is described by plane waves (like the motion of the centroid of any complex particle with internal degrees of freedom). Therefore, the dependence of the density of energy levels of a polaron's forward motion upon its kinetic energy has the same form as in the case of a free particle with a mass M and spin $\frac{1}{2}$.

The thermodynamically-equilibrial concentration of polarons is given by the usual formula:

$$n = \frac{2}{h^3} \cdot (2\pi M k T)^{\frac{3}{2}} \cdot e^{(\zeta - H_0)/kT},$$ (21')

where zeta ζ is the chemical potential of the electrons in the crystal. However the coefficient of the exponential factor is ordinarily many orders greater than in the case of electrons. Thanks to the interaction of polarons with thermal oscillations of ions, a Maxwellian distribution of the speeds of polarons is established.

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